

Discussion on the shortcoming of conventional RFCC riser reactor

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Introduction

In petroleum refining industry, the fluid catalytic cracking (FCC) process is one of the most important processes converting heavy oil into light products. Especially in China, it affords about 80% of gasoline and 30% of diesel oil in market. So increasing the yield of desired products and improving the product distribution is the eternal aim pursued by researcher and engineer in this field. But now it is faced with another baptism to satisfy the need for producing environmentally-cleaner gasoline and diesel fuels.

During the recent decade, most FCC processes were revamped into the RFCC (residue fluid catalytic cracking) processes for processing the heavier and heavier feedstock. According to the intuitive knowledge on the disadvantages of conventional FCC reactor, RFCC technology have been got great development around the reaction system, including the feeding atomization (nozzle), quick separation of oil vapor and spent catalyst, steam stripping of high efficiency, temperature control of reaction, as well as the innovation of riser reactor [1-3]. Except for the downer riser technology [4-7] and MSCC technology [8], the studies on the reactor technology of RFCC is scarce. In order to promote the progress of RFCC technology, it is much important to understand the shortcoming of the conventional riser reactor. This problem was discussed in this paper according to the experimental results, industrial test data, as well as literature information.

Experimental

Most researches about the reaction characteristics of RFCC were completed in the fixed fluidized-bed reactors, or with the small riser or downer reactor in laboratory. Because of the complex physical and chemical phenomena occurring in the RFCC reactor, the results obtained in laboratory only afford the limited information about the real situation in commercial unit. For understanding the reality occurring in industrial RFCC riser reactor, a special sampling system was developed, and the treatment and analysis procedure was established. The flow chart of the modified sampling system as shown in figure 1 includes tube sampling probe for catalyst and product (8), the small cyclone for the partial separation of catalyst and oil vapor (2), two stages of cooler of product oil vapor (3A and 3), two liquid product collectors (4A and 4), the wet gas meter for measuring the volume of the noncondensable gas (6), and the gas sample bag for analyzing the composition of the noncondensable gas product (7). The samples obtained from the riser consisted of gas, light liquid, heavy liquid product, and oily catalyst. The gas and liquid were handled and analyzed in a manner to determine their weights and composition. The oily catalyst was treated with different methods including the steam stripping and solvent extraction. The safety measures to be used in the sampling process using this sampling system refers to the previously published papers [9-10].

The sampling work was done in RFCC units of Shengli Petrochemical Factory and Qingdao Petrochemical factory, the sampling points on RFCC riser were selected in terms of the real situation of industrial unit and shown in figure 2.

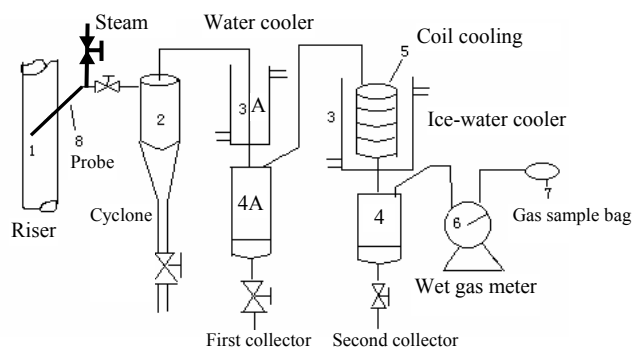


Figure 1. Flow chart of the sampling system for RFCC riser

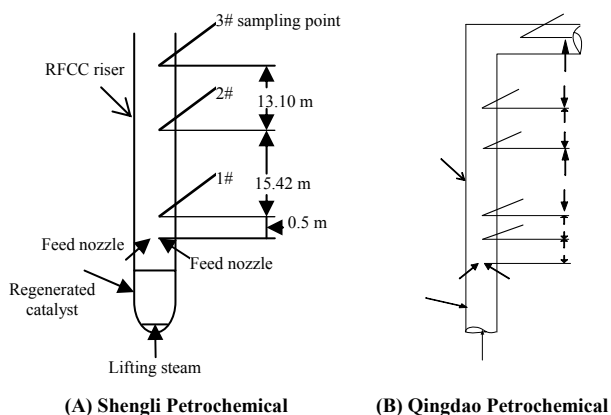


Figure 2. Illustration of sampling points on RFCC riser

Results and Discussion

From the literature, experimental results, and the sampling research of industrial RFCC units, at least three defects could be realized, that is, too long reaction time, too low average activity of catalyst, and the harmful competition of different reactants. These defects resulted in the worse product distribution and the lower once-through conversion.

Too long reaction time. Although the feedstock of RFCC is different from that of distillate FCC because of its high boiling point, high resin and asphaltene content, and high contaminant concentration, the riser reactor is the same for most RFCC with FCC process yet. In general, the distillate FCC is thought to be a gas-solid catalytic reaction, but gas, liquid, and solid exist simultaneously in reactor for RFCC. In catalytic cracking, the chemical bond rupture should mainly occur in the paraffin and naphthene hydrocarbons, the side chains of benzene ring, and the bridge bond between two cyclic structures. The larger the molecule of reactant is, the easier the cracking reaction happens, so the RFCC feedstock is easier to be cracked than distillate feedstock, then the RFCC process should need a shorter reaction time than the distillate FCC. This viewpoint has been accepted in petroleum refining for a long time, so the quick separation of oil vapor and spent catalyst, temperature control of riser reactor, and the MSCC technology were developed, and the downer reactor has been researching.

Gao Yongcan^[11] studied the thermal and catalytic cracking of VGO mixed with some AR and VR with ACE-Model-R small fixed fluidized-bed reactor, Xytel corporation. The reaction time, catalyst/oil ratio, and temperature are considered for their contribution to thermal and catalytic reaction, it is concluded that the

short contact time of oil and catalyst may suppress the detrimental thermal cracking reaction obviously.

The riser of 60×10^4 t/a RFCC unit in Shengli Petrochemical Factory is 48 m long, the studies on product distribution along the riser of RFCC show that the main conversion of feedstock to gasoline and diesel distillates is completed in the front stage of riser^[12]. At 1# sampling point (Figure 2(A)), only 0.5m from the feedstock nozzles, about 60% feedstock was converted into diesel and lighter compounds, the conversion of feedstock reaches about 80% at 2# sampling point. Figure 3 describes the variation of product distribution along the riser length of the RFCC unit. It means that the riser is too long to result in an ideal product distribution at the exit of riser.

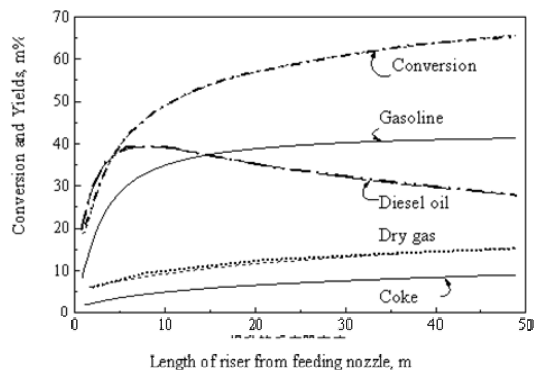


Figure 3. Conversion of feedstock and yields of products versus the length of riser (Simulated result of commercial RFCC unit^[13])

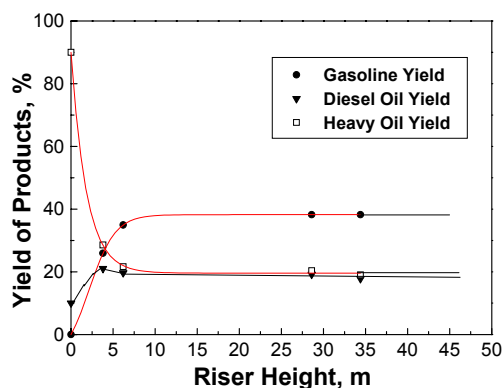


Figure 4. Product yields varies along the riser height

Fortunately the sampling work was perfectly completed in Qingdao Petrochemical Factory. The material balances at every sampling point (Figure 2(B)) were made in terms of gases and liquid products collected in sampling process, as well as the oil absorbed in oily catalysts. The product distribution at different sampling positions was shown in figure 4. The gasoline yield reaches its maximum point at the middle of riser, but the yield of diesel oil reaches its maximum point at the initial stage of riser. The remaining heavy oil ($>350^\circ\text{C}$) decreases along the riser at the bottom of riser, but has no notable change at the later half of riser. In another words, the change of product distribution is drastic in the initial stage of riser and tempered at the later half of riser. In the initial stage of riser, the heavy oil yield decreases from 90m% in feedstock to 28.9m% at the first sampling point (3.8m apart from the nozzles), and nearly 60m%

of feedstock are converted into gasoline, diesel oil, gaseous product and coke. This points again that the initial stage play a very important role in RFCC processing, and improving the contacting situation of feedstock with regenerated catalyst is a key method to get satisfied product distribution and maximum refinery profit.

From the results mentioned above, a much short reaction time than the present one (about 3 seconds) is enough for the RFCC riser to complete the conversion of heavy oil into diesel and gasoline distillates, gas and coke. For distillate FCC process, the same viewpoint would be derived from the previous researches. With a continuous, isothermal wall, transfer line catalytic cracking reactor, Paraskos and Shah^[14] studied the FCC reaction of mid continent gas oil at the catalyst/oil ratio of 4~8 and temperature of $510\sim 538^\circ\text{C}$. The conversion of mid continent gas oil into gasoline, gas and coke was plotted with the contact time of oil and catalyst in reactor as shown in figure 5, the contact time is calculated based on zero conversion of gas oil. Before 3 seconds of contact time, the conversion increases quickly, and then closes to a stable level. It could be deduced that 2 seconds of real contact time of oil vapor and catalyst is enough to convert gas oil into gasoline, gas and coke. In china, the diesel distillate in FCC process is also the desired product, a shorter reaction time than 2 seconds should be employed.

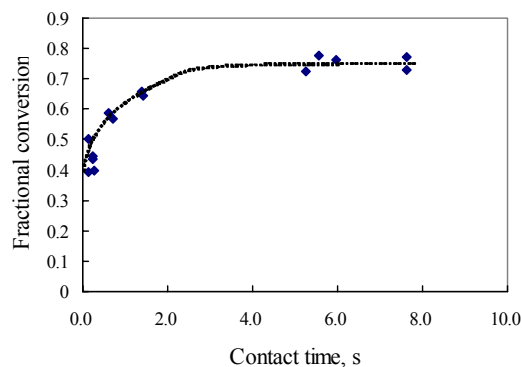


Figure 5. Conversion versus contact time in pilot apparatus

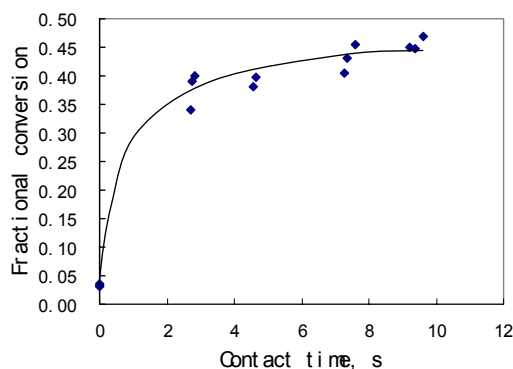


Figure 6. Conversion versus contact time in commercial FCC unit

In a commercial FCC riser of 30 meters long, the sampling was done by Shah and Huling^[15] through an open pipe probe using a specialized sampling technique at three probe positions: 8.8, 15.0, and 23.8 meters from the bottom of the riser. In this study, the feedstock is the blend of atmospheric gas oil and vacuum gas oil, the desired product is gasoline, the operation conditions is 6.6~7.1 for catalyst/oil ratio and $480\sim 520^\circ\text{C}$ for reaction temperature. According to the material balance at every sampling point, the similar

relationship between conversion of gas oil and the contact time was obtained as shown in figure 6, the conversion of gas oil cracking increases quickly at the initial stage of riser, and then slowly. It is shown again that the cracking reaction in FCC process occurs at the initial stage of riser.

For distillate FCC process and RFCC process, the conversion of feedstock into desired product is completed in very short time at the bottom of riser reactor, especially the diesel distillate is produced as a desired product in China. If the contact time is too long, the overcracking of diesel and gasoline is inevitable.

Low catalyst activity and poor selectivity. In FCC process, thermal cracking and catalytic cracking exist simultaneously, what is the dominant one depends on the catalyst properties and operation conditions (reaction temperature, catalyst/oil ratio, contact time). The catalytic cracking is the desired reaction for its good product selectivity. Too long contact time and too high reaction temperature will accelerate the thermal cracking, and lead to excessive light gas yield and lower desired product value. At the proper reaction temperature and contact time, the catalyst properties, especially the microactivity, is the key to intensify the catalytic cracking.

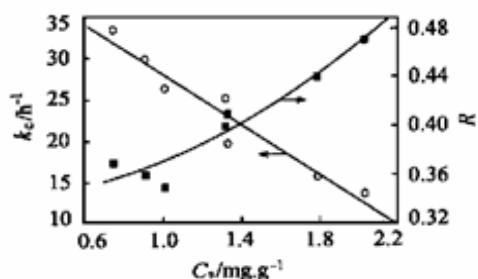


Figure 7. Effect of coke deposition on thermal cracking and catalytic cracking ^[11]

Gao Yongcan^[11] gave the effect of coke deposition in catalyst on thermal cracking and catalytic cracking as shown in figure 7. In figure 7, C_s is the coke content of catalyst (mg coke/ g catalyst); k_c is the overall reaction rate constant, represents the catalyst activity; and R is the ratio of (C_1+C_2) to $i-C_4$, the criterion of thermal cracking and catalytic cracking. With the increase of coke deposition on catalyst, the catalyst activity decreases gradually, the thermal cracking becomes more and more dominant, so the catalyst selectivity to desired product lowers.

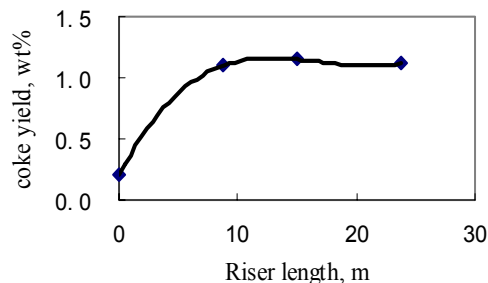


Figure 8. Coke content of catalyst versus riser length in commercial test ^[15]

For a commercial gas oil FCC process, Shah and Huling ^[15] obtained the curve of coke content of catalyst along the riser length through the in situ sampling at different position. From figure 8, coke

content of catalyst increases rapidly to a stable value at the front section, and then has no obvious change in the rear end of riser. According to the report from Gao Yongcan^[11], the catalyst activity will decrease quickly to a low level, and the thermal cracking become a more important reaction at the rear end of riser.

For commercial RFCC process, the changes of catalyst activity with riser length were obtained through the sampling work in Shengli Petrochemical Factory and Qingdao Petrochemical Factory. Figure 9 shows the curves of activity varying with riser height. In figure 9A, the catalyst activity falls down to a low level at the mixing zone of regenerated catalyst and feedstock, then increases slightly to a maximum, finally decreases gradually again. The average microactivity of catalyst in riser reactor is about 50% of the regenerated catalyst. In figure 9B, the microactivity of catalyst decreases to a stable value, and then maintain the level, no maximum exist. The average microactivity of catalyst in riser reactor is only 40% of the regenerated catalyst. Although the feed properties and the operation conditions influence the detail of activity evolution along the RFCC riser, the common result is the drastic fall of catalyst microactivity at the initial stage, the subsequent reactions in riser occur in the catalyst with low activity and poor selectivity.

Therefore, increasing the average microactivity of catalyst in RFCC riser reactor and improving its selectivity is one of the key problems to develop the new RFCC technology.

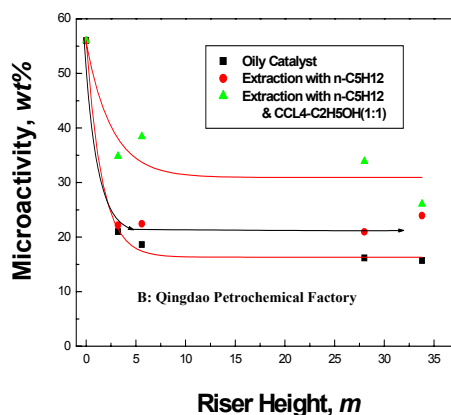
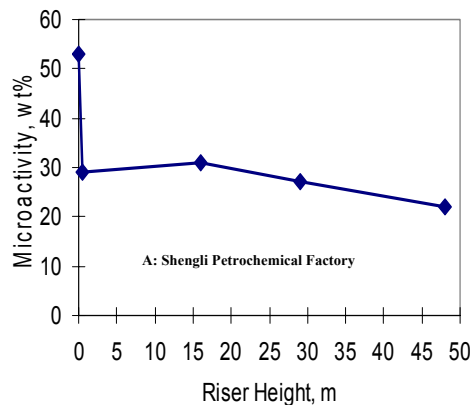


Figure 9. Catalyst microactivity versus riser length for RFCC units

Harmful competition of different reactants. In RFCC process, always there is the recycle oil to be piped into the riser reactor from the bottom of RFCC fractionation tower. The ratio of recycle oil to fresh feed is 0.1~0.8 depending on the feed properties and the

product scheme. The RFCC feedstock has a lot of heavy component with high boiling point, difficult to gasify and move into the interior surface of catalyst, but easy to subject to cracking reactions. Compared with the former, the recycle oil, mainly consisting of aromatics, has a narrow boiling range, so it is easier to gasify and move into the interior surface of catalyst, more difficult to react continuously. In the conventional RFCC process, the fresh feed and the recycle oil exist in one reactor, competition of adsorption on catalyst and chemical reaction will reduce the conversion of fresh feed and results in the unsatisfactory product distribution. So the ideal technology should make the fresh feed and the recycle oil to react respectively in two reactors with different conditions.

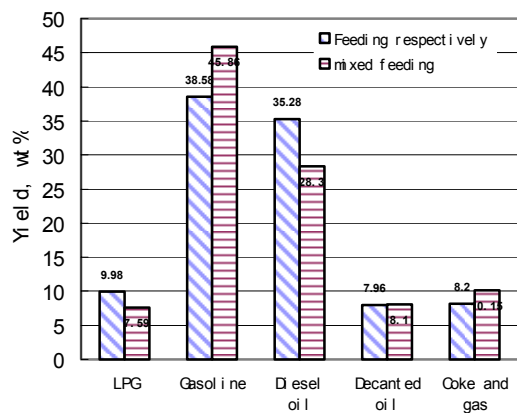


Figure 10. Influence of competition on FCC product distribution

A set of commercial distillate FCC data were shown in figure 10, the Feeding respectively presents the fresh FCC feed and the recycle oil to be injected into two different riser reactor at the different reaction conditions, and the Mixed feeding does the fresh FCC feed and the recycle oil to be injected into one riser reactor as a mixture. Compared with the conventional feeding, the feeding respectively can increase the conversion, obviously increase the ratio of diesel oil to gasoline, and decrease the yield of coke and dry gas.

Conclusions

From the literature, experimental results, and the sampling research of industrial RFCC units, three defects, that is, too long reaction time, too low average activity of catalyst, and the harmful competition of different reactants, were proposed and discussed. These defects resulted in the worse product distribution and the lower once-through conversion.

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